Redistribution of cations amongst different lattice sites in $Cu_{1-x}Co_xFe_2O_4$ ferrospinels during alkylation: magnetic study

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A series of $Cu_{1-x}Co_xFe_2O_4$ ($x = 0$, 0.25, 0.5, 0.75, 1.0) ferrospinels prepared by low temperature coprecipitation method and glycine nitrate combustion method has been studied in gas phase methylation of phenol. Phenol methylation gives mainly *o*-cresol and 2,6-xylenol as major products and among various compositions, $x = 0.50$ shows good catalytic performance irrespective of the preparation method. The difference in properties of the fresh and spent catalysts was thoroughly characterized by adopting various physico-chemical characterization techniques with special emphasize on magnetic measurements. Various conclusions derived from magnetic study are in good agreement with our previous study of XRD and Mossbauer on same catalyst system.

Redistribution of cations occurred during the reaction is evidenced from the increase of saturation magnetization in the spent. Spent $x = 0.0$ shows high T_c close to the value of Fe_3O_4 indicating that the material has ended with a solid solution of Fe_3O_4 and $CuFe_2O_4$ along with other reduced phases.

KEY WORDS: spinel; ferrites; $Cu_{1-x}Co_xFe_2O_4$; phenolmethylation; 2;6-xylenol; magnetic properties.

1. Introduction

Spinel ferrites have been used as effective catalysts for a number of industrially important reactions such as dehydrogenation of hydrocarbons, selective oxidation of butene to butadiene, treatment of automobile exhaust gases, oxidation of CO, H_2, methane etc. [1,2]. The interesting physical and chemical properties of spinel ferrites arise from the distribution of transition metal cations having various oxidation states, amongst the available tetrahedral and octahedral sites [3,4]. In ferrites, various oxidation states exhibited by the transition metal ions are either due to the intrinsic processes taking place during the synthesis or due to the catalytic reaction [5–8]. The cation distribution depends on the method of preparation of the compounds [9,10] as well as the processing parameters therein, such as the thermal history of the sample and the composition [11–13].

Ternary spinel systems like $Cu_{1-x}Co_xFe_2O_4$ are quite vulnerable during a catalytic process since the Fe^{3+} ion can be rearranged between its octahedral and tetrahedral sites [14]. Moreover the lack of specific site preference of both the Co^{2+} and Cu^{2+} results in an inverse or a partially inverse spinel, which leads the distribution of all the three ions among tetrahedral or octahedral sites in a quite complex manner [15–17]. Recently, we have successfully employed low temperature co-precipitation method for the synthesis of $Cu_{1-x}Co_xFe_2O_4$ catalyst system and these catalysts are found to be highly active towards *ortho*-methylation of phenol [18–21]. The advantage of low temperature synthesis procedure lies in the fact that Bronsted acid sites can be created in different cationic environment together with the Lewis acid sites and this property makes them as typical active and selective catalysts for various acid catalyzed organic transformations [22,23].

Catalyst deactivation and its regeneration is an important part in catalytic studies that demand careful analysis of the cause of deactivation during the catalytic reaction. Hence a series of complementary characterization techniques had been employed on the $Cu_{1-x}Co_xFe_2O_4$ catalyst system and these studies reveal the redistribution of transition metal ions on the available sites during the catalytic process of phenol methylation reaction [20,21]. To supplement these observations, we report in the present communication, magnetic studies on both fresh and spent catalysts and a correlation is arrived with our earlier findings. Moreover, we extended the magnetic studies on same series of compositions prepared by glycine nitrate combustion method and compared the results with corresponding compositions prepared by precipitation method. Although combustion method is a high temperature preparation technique, the structural changes occurring after the catalytic reaction are comparable with those of the coprecipitated catalysts showing the changes are not related to the specific surface area. Even though, literature shows some reports on the catalytic activity of Cu- and Co–ferrite systems, to the best of our

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knowledge for the first time magnetic properties are used with other characterization techniques for analyzing the redistribution of ions during catalysis.

2. Experimental

2.1. Preparation of the catalyst material

In order to get an insight into the catalyst behavior, two synthesis methods *viz*., the co-precipitation and the glycine nitrate combustion method were opted for various compositions of the series Cu_{1-x} $Co_xFe_2O_4$.

2.1.1. Precipitation method

The ferrospinel system having the general formula $Cu_{1-x}Co_xFe_2O_4$ ($x = 0$ to 1) were prepared by co-precipitation technique as described in our earlier publications [18–21]. Briefly, stoichiometric amounts of premixed metal nitrate solutions were rapidly added to an NaOH solution at room temperature under continuous stirring. Final pH of the resulting solution was adjusted between 9.5 and 10. Aging of the precipitate was carried out for 8 h and then washed well with demineralized water till free from both Na^+ and NO_3^- ions. The precipitates were filtered and dried at 80 °C in an air oven for about 36 h. Finally, the dried materials were powdered and calcined at 500 °C.

2.1.2. Glycine nitrate combustion method

The synthesis of $Cu_{1-x}Co_xFe_2O_4$ system by glycine nitrate method was done accordingly by a procedure reported by Chick *et al.* [24]. This method utilized the complexing behavior of glycine towards the metal ions in aqueous solution. In a typical synthesis procedure, stoichiometric amount of metal nitrates and glycine were dissolved in a glass beaker and are stirred vigorously to make it a homogeneous mixture. To the homogeneous solution, few drops of conc. HNO_3 were added and the resulting solution was boiled to evaporate the excess water on a hot plate. The viscous liquid was then ignited to underwent a self-sustaining combustion producing an ash composed of the oxide product. The formed material was then calcined at 500 °C for 5 h.

2.2. Catalytic activity measurements

Vapor-phase alkylation of phenol with methanol was performed at atmospheric pressure in a fixed bed, vertical, down-flow, integral silica reactor placed inside a double-zone furnace supplied by Geomechanique, France. Before carrying out the reaction, the catalyst was activated in a flow of dry air at 500 °C for 6 h and then cooled to the desired reaction temperature in presence of nitrogen. The liquid reactant mixture was fed by syringe pump (ISCO, MODEL 500D) at a weight hourly space velocity of 0.869 h^{-1} for all the measurements reported in this paper. The products of the reaction were condensed and then analyzed by GC, GC–MS and GC–IR. The spent catalysts were obtained after 10 h of the reaction at optimized conditions.

2.3. Physico-chemical characterization

The chemical composition, surface area, TG–DTA, TPR, Mössbauer and XRD parameters such as crystallite size and unit cell dimension of fresh as well as spent catalysts prepared by coprecipitation method have already been reported in our earlier studies [20,21]. X-ray diffraction (XRD) patterns of the calcined powder catalysts (fresh) and the used catalysts (spent) were recorded to verify the phase purity using a Rigaku Geigerflex instrument equipped with CuK_α radiation ($\lambda = 1.5405$ Å) with Ni-filter. X-ray diffractograms of the fresh and the spent catalysts prepared by co precipitation and combustion method are shown in figures 1 and 2, respectively. The IR spectrum of the ferrite samples were recorded through a DR mode (Shimadzu) in the range 400–1000 cm^{-1}. The magnetic properties of the samples, fresh as well as spent, were measured on EG & G PAR 4500, vibrating sample magnetometer (VSM). Saturation magnetization was measured at a magnetic field of 15 kOe, while the temperature dependence of magnetization was measured in the range of 200–600 °C.

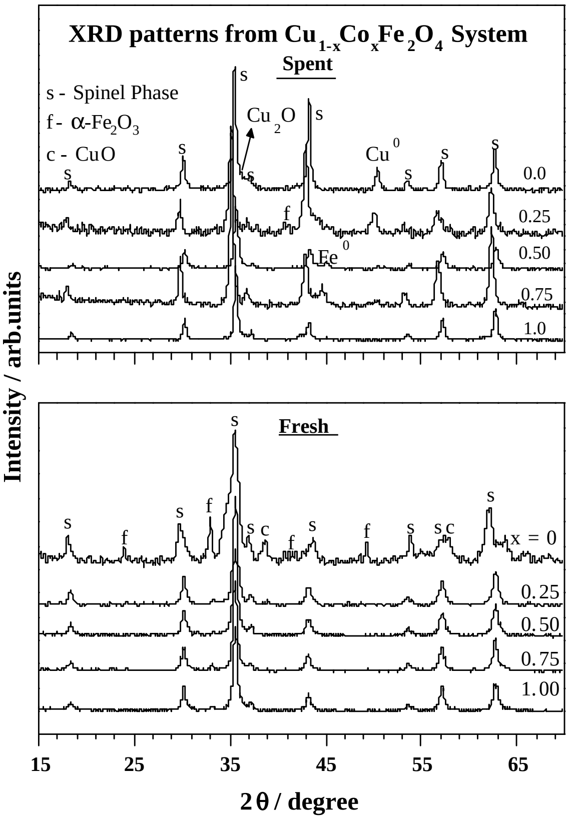

Figure 1. X-ray diffractograms of fresh (bottom panel) and spent (top panel) ferrospinel $Cu_{1-x}Co_xFe_2O_4$ catalysts prepared by coprecipitation method. XRD from spent catalysts are after phenol methylation reaction at 350 °C for 10 h with 1:5 composition of phenol–methanol.

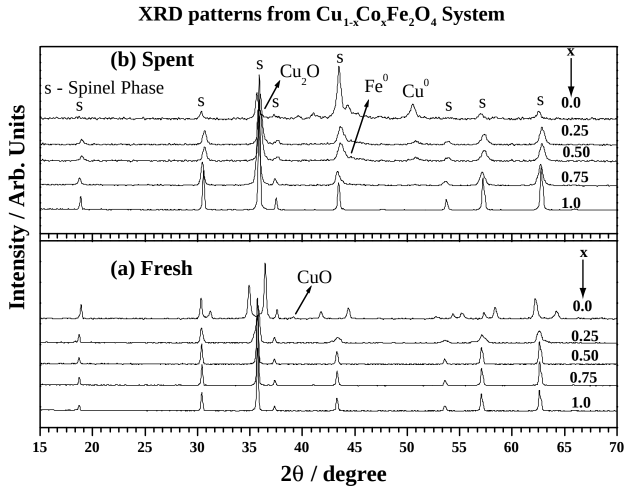

Figure 2. X-ray diffractograms of fresh (bottom panel) and spent (top panel) ferrospinel $Cu_{1-x}Co_xFe_2O_4$ catalysts prepared by glycine nitrate combustion method. XRD from spent catalysts are after phenol methylation reaction at 350 °C for 10 h with 1:5 composition of phenol–methanol.

3. Results

3.1. Catalytic activity

Reaction of phenol with methanol gave a mixture of *ortho*-methylated products, *viz*., *o*-cresol and 2,6-xylenol as major products and anisole, 2,4-xylenol, *p*-cresol and 2,4,6-trimethyl phenol altogether in 0.5–2.5% range as side products over $Cu_{1-x}Co_xFe_2O_4$ prepared by coprecipitation method. The optimum reaction parameters with respect to temperature, methanol/phenol mole ratio and space velocity are 350 °C, 5 and 0.869 h^{-1}, respectively. It was found that compositions containing both Cu and Co are more active than end compositions, *viz*., $CuFe_2O_4$ and $CoFe_2O_4$, in terms of phenol conversion and 2,6-xylenol selectivity. Additionally, among various intermediate compositions, $x = 0.50$ shows maximum catalytic performance. For example, though all the compositions show more than 80% conversion under optimized conditions, it is found that $x = 0.50$ is active even at lower temperature. Thus nearly 80% phenol conversion is achieved even at 280 °C with $x = 0.50$ composition and at optimized temperature it is increased to 97%.

On the contrary, the catalysts synthesized by glycine nitrate combustion method had shown a tremendous decrease in the activity behavior, which further supports the influence of method of preparation of catalysts for a designed reaction. Comparison in the catalytic activity behavior of catalysts prepared by both methods is depicted in figure 3. Even though the conversion and 2,6-xylenol selectivity is reduced for the glycine nitrate prepared catalysts, the nature in catalytic performance and catalysts deactivation are similar to that of the co-precipitated samples and a maximum conversion is obtained for the catalyst of composition $x = 0.50$.

3.2. Characterization

3.2.1. XRD

The phase purity and the degree of crystallinity of the catalysts before and after the reaction were analyzed by XRD. Figures 1 and 2 compares the X-ray diffractograms of the fresh and the spent catalysts prepared by coprecipitation and combustion method, respectively, and the various results obtained are summarized in table 1. From the figure, it is clear that the characteristic reflections of spinel phases are independent of the preparation method opted and the lattice parameters

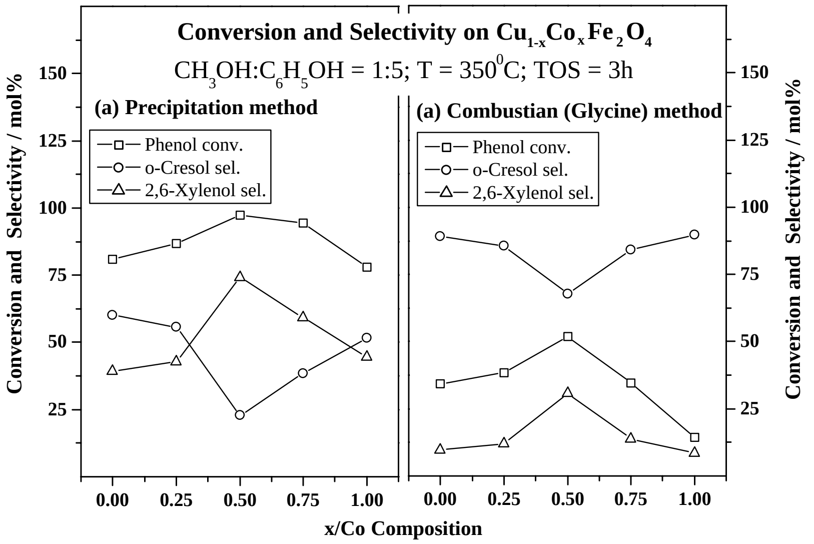

Figure 3. Composition dependence of phenol conversion and products selectivity in mol% on $Cu_{1-x}Co_xFe_2O_4$ prepared by coprecipitation (a) and glycine nitrate combustion method (b). Phenol methylation is carried out with phenol–methanol composition of 1:5 at 350 °C and at WHSV of 0.869 h^{-1}. Conversion and selectivity values are at $t = 3$ h.

Table 1
Identification of extra phases on $Cu_{1-x}Co_xFe_2O_4$ (x = 0, 0.25, 0.5, 0.75 and 1) for both fresh and spent samples

Composition (x)	Sample type	Phases ('d' value)				
		α-Fe_2O_3	CuO	Cu_2O	Metallic Cu	Metallic Fe or iron carbide
0.00	Fresh	3.71	2.32[a]			
		2.71	1.59			
		2.21	1.37			
		1.84				
	Spent			2.47[a]	1.81[a]	
0.25	Fresh	2.71 (trace)	2.32 (trace)			
	Spent			2.47[a]	1.81[a]	2.03 (trace)[a]
0.50	Fresh					
	Spent		2.32		1.81[a]	2.03[a]
0.75	Fresh					
	Spent					2.03[a]
1.00	Fresh					
	Spent					

[a] Denotes peaks are present also in the XRD pattern of samples prepared by glycine nitrate combustion method.

are in well agreement with the ASTM card data (ASTM card no. 1-1121 and 3-0864, JCPDS card no. 3-864, 22-1086) and other literature reports [25,26]. However, the fresh Cu-rich catalysts ($x = 0$) prepared by coprecipitation method exhibits diffraction pattern characteristic of cubic phase with considerable amounts of unreacted Fe_2O_3 and CuO phases. But the substitution of Cu by Co leads to the formation of well-defined spinel phases and the additional reflections observed in the earlier case are hardly detected at $x \geq 0.25$ compositions. The fresh $x = 0$ composition prepared by glycine nitrate combustion method shows the presence of tetragonal spinel phase with trace amount of CuO, while the rest compositions show cubic spinel phase without any impurity.

XRD of spent catalysts shown in figures 1 and 2 also displays all characteristic reflections and ascertain the integrity of the spinel structure. Spent catalysts show additional phases of Cu_2O and metallic Cu and Fe. In the case of $CuFe_2O_4$, diffractogram shows the presence of metallic Cu and Cu_2O phases. These results indicate the formation of a reductive atmosphere on the catalyst surface due to the decomposition of methanol. The XRD patterns of the spent catalysts for compositions $x = 0.25$, 0.5 and 0.75 show reflections of Cu_2O, metallic copper and zerovalent iron (mostly as iron carbide) in addition to the spinel phase. However the extent of reduction decreases as the Co content increases. In contrast to the Cu containing spinels, the diffraction peaks of the spent $CoFe_2O_4$ were almost unchanged with respect to those before test.

3.2.2. FTIR

IR studies were carried out on both fresh and spent samples of coprecipitation method to understand the band positions attributed to the lattice sites. Since, in spinels metal ions are distributed in two different environments, the spinel phase formation can be very well assigned by the appearance of two broad IR bands. In the present study, the absorption bands for the series of Cu–Co ferrites are expected to be in the close frequency range due to the inverse nature of all the compositions. The DR-IR spectra of both fresh and

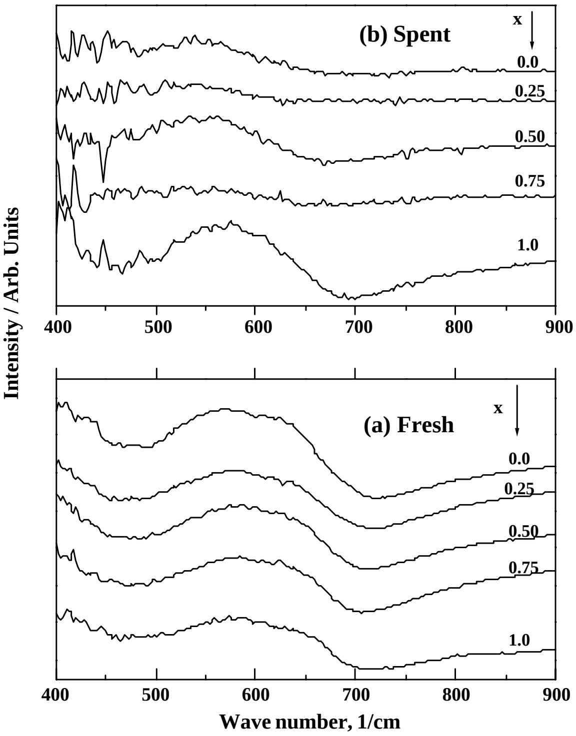

Figure 4. FTIR patterns of fresh (bottom panel) and spent (top panel) ferrospinel $Cu_{1-x}Co_xFe_2O_4$ catalysts prepared by coprecipitation method. IR from spent catalysts are after phenol methylation reaction at 350 °C for 10 h with 1:5 composition of phenol–methanol.

spent samples prepared by coprecipitation method are presented in figure 4. All the compositions of the system showed two strong IR bands, v_1 and v_2 around 710 and 460 cm^{-1}, respectively. Differences in $M–O^{2-}$ bond distances for the octahedral and tetrahedral sites leads to the difference in the two band positions. Waldron [27] and White and De Angelis [28] attributed the high frequency band around 710 cm^{-1} to the intrinsic vibrations of the tetrahedral group and the lower frequency band at 460 cm^{-1} to that of the octahedral group. According to Waldron, tetrahedral bonds have the effect of substantially increasing the frequency of vibration, since these cations introduces a supplementary restoring force in a preferential direction along the $M_{tet.}$-o bond.

In the spectra of spent samples the following important features are observed,

(a) The intensity of both tetrahedral and octahedral bands decreases on spent catalysts compared to the corresponding fresh one and it is observed on all Cu containing samples.
(b) Splitting of octahedral bands is observed on spent samples whereas the tetrahedral band remained as such though the latter intensity is reduced with respect to the fresh sample.
(c) The above two effects, that is the decrease of intensity as well splitting of octahedral bands, were less affected on the spent sample of $CoFe_2O_4$.

FTIR spectra of spent samples revealed that catalyst on reaction ended with several phases other than spinel phase, which is in well agreement with the results of XRD and Mossbauer results. The presence of reduced ions in the spinel lattice as well other segregated phases cause the splitting of absorption bands while the local lattice deformations occurs due to the presence of reduced ions and extra phases, which can lead to a noncubic component in the crystal field potential and to the splitting of the band [29,30].

3.2.3. Magnetic properties

In order to further confirm the results obtained with XRD and Mossbauer, magnetic measurements were measured on fresh and spent samples, using a VSM. Figures 5 and 6 demonstrates the change in magnetization (M) with the applied magnetic field (H) for various compositions of $Cu_{1-x}Co_xFe_2O_4$ prepared by coprecipitation and combustion method, respectively. Table 2 gives the data of saturation magnetization (M_s) obtained for both the techniques. The important feature derived from figure 5 and 6 and table 2 are: (i) saturation magnetization (M_s) increases with Co percentage for the fresh sample prepared by both methods; (ii) spent catalysts show a higher saturation magnetization than the respective fresh compositions and the increase is predominant on $x \leq 0.25$ and (iii) glycine combustion method results an increased saturation magnetization than their corresponding fresh composition prepared by coprecipitation method.

The magnetic transition temperature (Curie temperature, T_c), recorded in the range 200–600 °C, further demonstrates the temperature dependence of magnetization for fresh and spent catalysts for both methods and is shown in figures 7 and 8. The gross picture of T_c values for both the methods is given in table 3. The important observations regarding the trends in the T_c are: (i) T_c was increased with Co percentage for fresh catalysts irrespective of the preparation method; (ii) T_c of fresh catalysts is in the same range for both types of catalysts obtained by glycine and coprecipitation method and (iii) T_c is higher (530–580 °C) for the spent

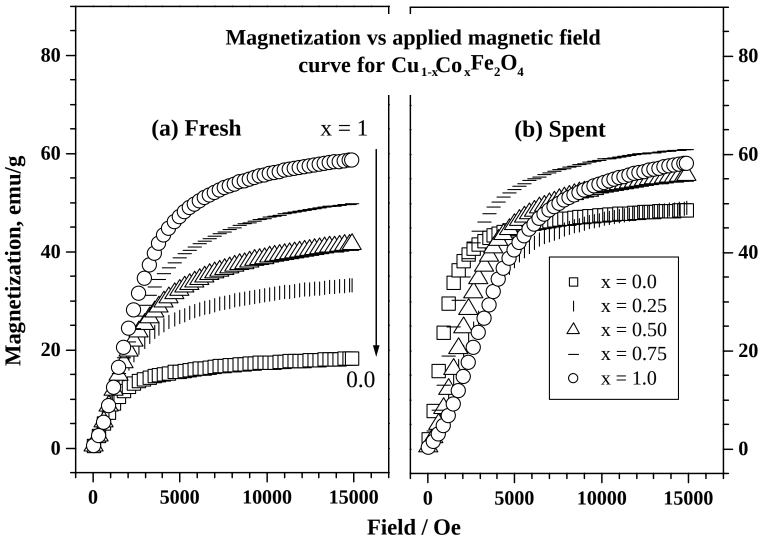

Figure 5. Variation of magnetization with applied magnetic field for fresh and spent $Cu_{1-x}Co_xFe_2O_4$ catalysts prepared by coprecipitation method.

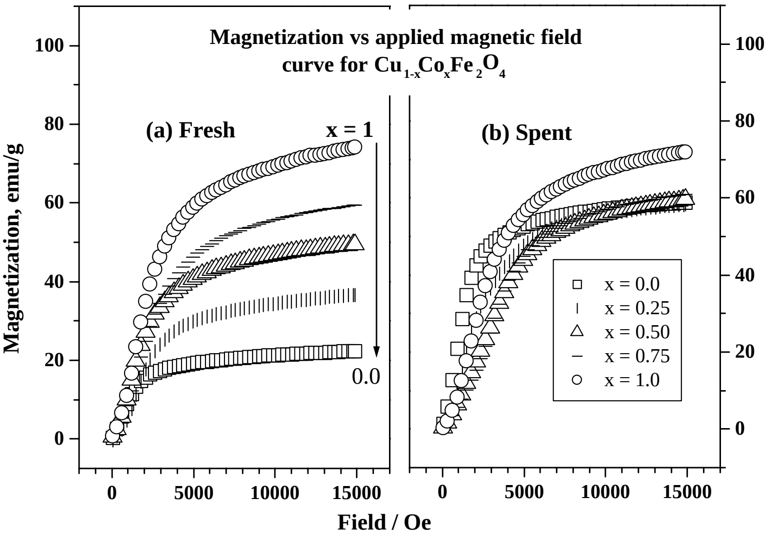

Figure 6. Variation of magnetization with applied magnetic field for fresh and spent $Cu_{1-x}Co_xFe_2O_4$ catalysts prepared by glycine nitrate combustion method.

Table 2
Saturation magnetization, M_s emu/g for various compositions of $Cu_{1-x}Co_xFe_2O_4$ ($x = 0, 0.25, 0.5, 0.75$ and 1) catalysts

Composition (x)	Preparation method			
	Coprecipitation		Glycine nitrate (combustion)	
	Fresh	Spent	Fresh	Spent
0.00	18.2	48.6	24.6	61.1
0.25	33.2	49.1	36.6	58.6
0.50	41.5	55.7	49.4	60.9
0.75	49.8	61.0	59.5	58.5
1.00	58.6	60.4	74.2	71.1

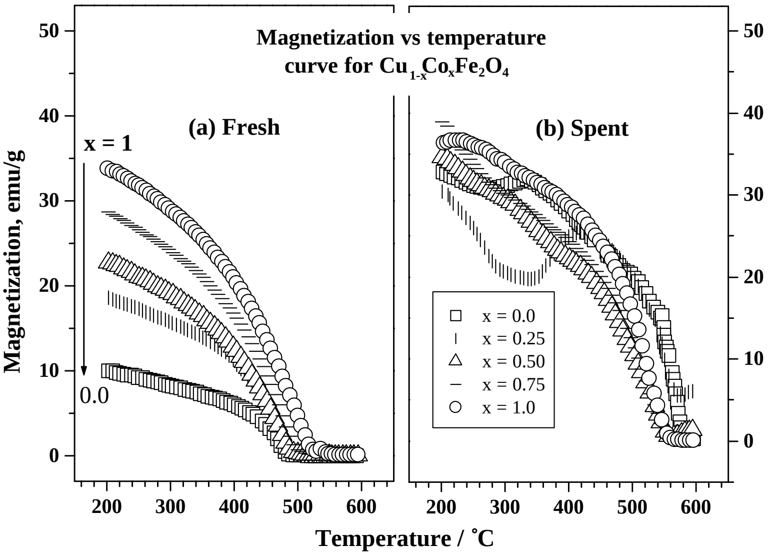

Figure 7. Variation of magnetization with temperature for fresh and spent $Cu_{1-x}Co_xFe_2O_4$ catalysts prepared by coprecipitation method.

catalysts than the respective fresh ones. However, the increase in T_c is pronounced on $x \leq 0.25$ and there is a conspicuous drop in magnetization around 250–350 °C for the same composition.

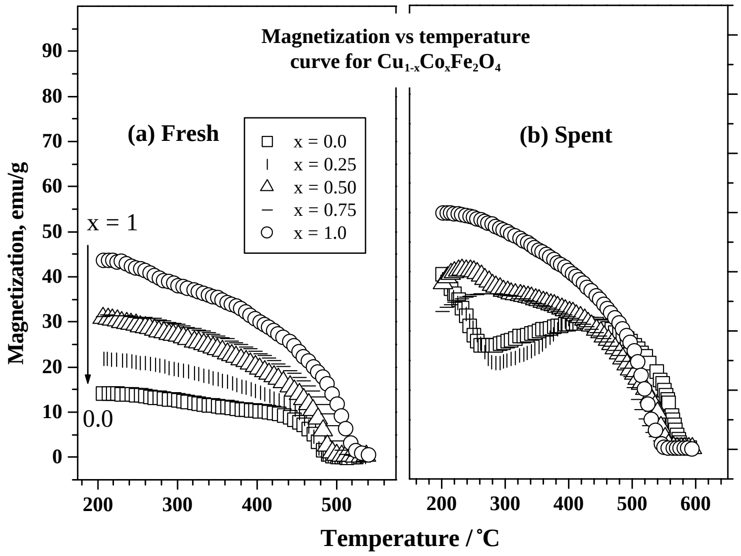

Figure 8. Variation of magnetization with temperature for fresh and spent $Cu_{1-x}Co_xFe_2O_4$ catalysts prepared by glycine nitrate combustion method.

Table 3
Curie temperature, T_c (°C) for various compositions of $Cu_{1-x}Co_xFe_2O_4$ (x = 0, 0.25, 0.5, 0.75 and 1) catalysts

Composition (x)	Preparation method			
	Coprecipitation		Glycine nitrate (combustion)	
	Fresh	Spent	Fresh	Spent
0.00	484	580, 300	489	577, 260
0.25	483	568, 276	484	565, 280
0.50	490	555	490	558
0.75	500	551	509	538
1.00	523	554	527	535

4. Discussion

From the reaction data it is clear that the compositions containing both Cu and Co are more active than the end compositions ($x = 0$ and 1.0) and the effect of Cu is more pronounced than Co towards phenol methylation. Examination of the spent catalysts by XRD revealed that considerable structural changes have occurred on Cu rich samples during the course of the reaction. Spent catalysts show predominant spinel phase along with additional phases of Cu_2O, metallic Cu and Fe. This indicates the reductive atmosphere under methylation conditions, which resulted in loosing the structural integrity to some extent for $x = 0.0$. Such reduction is quite possible, because methanol acts as a reducing agent through two simultaneous pathways, the methylation of phenol and decomposition of methanol itself. These reactions produce H_2, CO and aldehydes as reducing species while oxidizing compounds such as CO_2 and acetic acid are also present in the gas phase. Thus the reaction resulted in segregation of various other phases along with spinel phase as pointed in table 1. However the nature of segregated species and its concentration essentially depend on composition and reducing atmosphere.

Nevertheless, the structural integrity is retained high at $x = 1$ as confirmed from XRD. The observation is in well agreement with the nature of heat of formation of the two compounds namely $CuFe_2O_4$ and $CoFe_2O_4$ [31]. It is found that the process $CuO + Fe_2O_3 \rightarrow CuFe_2O_4$ is endothermal (+21.2 kJ), and thus spontaneous $Cu_2O + Fe_3O_4$ phase separation may take place during the reaction. Whereas the $CoO + Fe_2O_3 \rightarrow CoFe_2O_4$ being exothermal (−24.7 kJ), such process is not expected for $CoFe_2O_4$. Thus the reducing atmosphere during the catalysis has resulted in the formation of Fe_3O_4 phase for $x = 0$, which cannot be distinguished by XRD due to overlapping "d" values of $CuFe_2O_4$ spinel phase.

The present study on the IR spectra of the spent samples reveal that the absorption band around 460 cm^{-1} is splitted and it is possible to assume that catalytic reaction caused severe changes on octahedral sites. Thus the presence of reduced ions such as Fe^{2+}, Cu^{+} etc. on octahedral site is evidenced by its band splitting. On the other hand reaction did not cause any splitting of tetrahedral band even though its band intensity is slightly decreased which indicates reaction hardly affects the overall status of the tetrahedral sites. However this does not mean that migration of ions between tetrahedral and octahedral sites is not occurred during the course of the reaction. For example reduction of Fe^{3+} ion might be occurred on both tetrahedral and octahedral sites, however, the reduced Fe^{2+} ion preferably occur on octahedral sites by considering factors such as crystal field stabilization energy, Madelaung constant etc. [3,4,17].

Due to the lower coordination number of the tetrahedral cations, the attractive force for a single tetrahedral M–O bond will be strong. Since each octahedral cation is surrounded by more number of anions, the octahedral M–O bond will be weaker and hence will be more polar. Additionally, using low energy ion scattering (LEIS), a technique that is sensitive to the outer most atomic layer, Jacobs *et al.* [32] revealed that spinel surface sites are mainly octahedral and, hence, the octahedral cations are mainly exposed on the surface while Narasimhan and Swamy [14] reported that weak octahedral M–O bonds act as strong alcohol adsorption centers. Our own earlier catalytic studies and Mossbauer studies on these system revealed that the reduction of iron in the octahedral sites is clearly occurred in each sample up on the exposure to the reaction mixture. On the other hand, the reaction hardly influences the state of iron located in the tetrahedral sites. All these observations help us to conclude that the octahedral sites are the main centers for organic molecule adsorption, which causes the reduction of respective ions more on octahedral sites than on tetrahedral and hence pronounced splitting of octahedral bands is observed in the IR spectrum.

4.1. Magnetic properties

The information obtained from magnetic properties is in concurrence with the Mössbauer data reported in our previous publication [20]. In order to analyze the magnetic properties and to further correlate the changes in cation distribution, the saturation magnetization (M_s) is thoroughly evaluated. The cation distribution in mixed Cu–Co ferrospinel having the formula $Cu_{1-x}Co_xFe_2O_4$ can be expressed as

$$Fe^{3+}_{1-a-b}Co^{2+}_{a}Cu^{2+}_{b}[Co^{2+}_{x-a}Cu^{2+}_{1-x-b}Fe^{3+}_{1+a+b}]O_4$$

where x varies between 0 to 1 in the present study, while a and b are the fraction of Co and Cu ions in the tetrahedral sites and these values further depend on the preparation methods and on the processing conditions and/or may gets modified during the catalytic process. The saturation magnetic moment of spinel ferrite can be expressed as, $M_s = |M_B - M_A|$, where M_A and M_B are net magnetic moment of A (tetrahedral site) and B sublattice (octahedral site), respectively. Assuming that the Neels hypothesis is obeyed by the spinel systems and the spin only magnetic moments for Fe^{3+}, Co^{2+} and Cu^{2+} are 5, 3, and 1 μ_B, respectively, the net magnetic moment can be further modified as $(1 + 2x + 4a + 8b)\ \mu_B$ [33].

The above equation emphasizes the influence of a, b and/or x values on the magnetic moment of the catalyst and the increase of either of this value leads to an increase in the magnetic moment. Thus, as the percentage of Co increases from 0.25 to 1, the M_s value gets increased, irrespective of the preparation method. Similarly, an increase of a and/or b shift the magnetization value to higher side explains high M_s value for spent catalysts than the respective fresh ones. As Cu/Co occupies more tetrahedral sites, it forces an equivalent amount of Fe^{3+} to the octahedral sites, resulting an increase in the M_s value. This increase in M_s value implies aptly that, redistribution of cations is occurred during the reaction in such a way that the degree of inversion of the spinel decreases in case of spent catalysts. Thus preferential filling of Co and/or Cu ions to the tetrahedral site is occurred during the course of the reaction. These observations are in well agreement with the Mössbauer data showing a lesser number of tetrahedral Fe^{3+} ions in the spent catalysts compared to the fresh ones. For the Cu rich samples, Cu^{2+} being a Jahn–Teller ion, further force itself to occupy the tetrahedral sites in order to reduce the tetragonal distortion. In addition, part of the Fe^{3+} ions in the octahedral sites are converted to Fe^{2+} and even to metallic iron resulting a further modification in the net magnetic moment [34]. For the sake of charge balance in the spinel, either the cations should increase their valence or oxygen nonstoichiometry should result. Special attention had given for the Cu rich samples due to its interesting nature in magnetic behavior ($>M_s$) of the spent catalysts. It is found that the increase in M_s value from fresh to spent is more conspicuous for Cu rich samples. This discrepancy may be related to the formation of Fe_3O_4 species during catalysis since some of the Fe^{3+} ions are converted to Fe^{2+} ions and the spent catalyst may turn out to be a solid solution of $CuFe_2O_4$ and Fe_3O_4. These observations are also evident from the XRD and Mössbauer measurements. The appearance of CuO and Cu_2O lines and the disappearance of α-Fe_2O_3 lines in the XRD indicate partial conversion of $CuFe_2O_4$ to Fe_3O_4 and copper oxides is occurred. The obtained higher M_s value of Fe_3O_4 (92 emu/g) at 20 °C is far more than that of $CuFe_2O_4$ (25 emu/g) [30], which in turn reflects an increase in the M_s value for the spent catalysts.

The third observation of increase in the magnetization values for samples synthesized by glycine method also can be explained on the basis of difference in the cation distribution. Since the cation distribution is sensitive to the method of preparation [9], it is fairly assumed that the spinels prepared by glycine method are less normal than those prepared by coprecipitation method but more detailed study is needed in this respect.

The T_c reported in the literature for $CuFe_2O_4$, $CoFe_2O_4$ and Fe_3O_4 are 455, 520 and 585 °C, respectively [35]. T_c of spent samples is more than that of fresh samples and increase of Co concentration cause a shift towards the T_c of pure $CoFe_2O_4$, irrespective of preparation method. The increase is more conspicuous for copper rich samples and hence it is a clear evidence for the strong A–B super exchange interaction in the spent catalysts. The presence of Fe_3O_4 phase in the spent, as confirmed from XRD and Mössbauer spectra for copper rich samples, may increase their T_c values close to Fe_3O_4 (585 °C) rather than that of $CuFe_2O_4$ (455 °C). Further investigations are going on to verify the observed discrepancies and to analyze the drop of M_s value in the range 250–350 °C for Cu rich samples.

5. Conclusions

A series of $Cu_{1-x}Co_xFe_2O_4$ ($x = 0$, 0.25, 0.5, 0.75, 1.0) ferrospinels prepared by low temperature coprecipitation method and glycine nitrate combustion method has been studied in gas phase methylation of phenol. Notable differences have been observed in the catalytic performance between both methods and samples resulted from coprecipitation method exhibit more phenol conversion and 2,6-xylenol selectivity than the respective composition of combustion method and among which $x = 0.50$ shows the highest catalytic activity. Examination of the spent catalysts by XRD, IR and Mössbauer revealed that considerable structural changes have occurred on Cu rich samples during the course of the reaction. IR spectra of the spent samples reveal that the absorption band around 460 cm^{-1} is splitted well on Cu containing samples indicate octahedral sites are the main active centers for the reaction. Magnetic measurements shows an increase in M_s value in the spent catalysts which suggests, redistribution of cations is occurred during the reaction, which ultimately result preferential filling of Co and/or Cu ions in the tetrahedral site. Higher saturation magnetization value for sample synthesized by glycine method illustrate cation distribution is sensitive to method of preparation. Unexpectedly, spent $x = 0.0$ shows high T_c close to the value of Fe_3O_4 indicate the material is ended with a solid solution of Fe_3O_4 and $CuFe_2O_4$ along with other reduced phases. Structural changes happened during phenol methylation is alike irrespective of the preparation method and it is clearly evidenced from their similar behavior of magnetic properties.

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